INVESTIGATON OF SORPTION OF POTENTIAL ANTHROPOGENIC POLLUTANTS ON OIL SHALE AND ITS COMPOSITE FORMS

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Abstract

Sorption of three different asymmetric polar organic compounds – TEBA (benzyltriethylammonium chloride), Supragil WP (sodium diisopropyl naphthyl sulfonate) and 4-nitrophenol – was studied on Hungarian oil shale and its special composite forms. These frequently used and persistent chemicals can become anthropogenic pollutants when they get into the environment. Sorption is an appropriate method to remove these chemicals by oil shale, but the difficulty of the usage of oil shale as a sorbent is its crumbling nature. Therefore two different types of composites (oil shale–alginate and oil shale–agar) were prepared, which are more manageable, and their sorption abilities were compared to the oil shale powder. The sorbed amount of Supragil WP and 4-nitrophenol on oil shale in the oil shale–alginate composite was higher than on powder, while the sorbed amount of TEBA on oil shale in the oil shale–agar composite was almost the same as on powder.

Introduction

Oil shale is a rock of natural origin containing no artificial chemicals, which is present in a large amount in the world, also in Hungary. Oil shale originates from the biomass of algae accumulated in the volcanic craters over 4 to 5 million years. It is widely used in agriculture as a soil-ameliorating agent because of its organic and microelement contents and low price. Usually its organic material content is between 5 and 50 %, but in some deposits the content can reach 90 %, which is mainly kerogen [1]. Unfortunately oil shale is easily crumbling, which inhibits its practical usage as a sorbent. Its sorption abilities for removing pollutants has already been investigated [1-3].

Alginate is a biopolymer, it is extracted from brown algae. It consists of 1,4-linked β-D-mannuronate and α-L-guluronate. The ratio of mannuronate and guluronate fractions depends on the source of the alginate, thus the physical and chemical properties of alginate vary in wide ranges. In the presence of some divalent cations (such as Ca^{2+}, Sr^{2+}, Ba^{2+}), the linear copolymer chains change to gel form, these cations crosslink the alginate chains [4-5]. Alginate has been used for removing environmental pollutants [6].

Agar is also a natural polysaccharide, a biopolymer, which derives from cell wall of red algae. Agar can be fractionated into two components: agarose and agaropectin. The agarose fraction has greater gelling capability. It consists of 1,3-linked β-D-galactopyranose and 1,4-linked 3,6-anhydro-α-L-galactopyranose. These repeating units form long chains. Agaropectin has essentially the same backbone structure, but with various amounts of the residues replaced by pyruvic acid ketal and different sugar units. The gel liquefies when heated and it binds when

cooled. The random coils in solution change to bundles of helixes in gel form [5,7]. Agar has also been used for eliminating chemical pollutants [8].
The relatively high price of alginate and agar (compared to the oil shale) disadvances the wide usage. The combination of alginate or agar with the lower-cost oil shale sorbent results in a new composite material, which could eliminate pollutants as effectively as the oil shale powder can.
TEBA (Figure 1, left) is a popular cationic phase transfer catalyst at organic chemical syntheses, Supragil WP (Figure 1, middle) is an anionic chemical, which is widely used as a dispersant, while 4-nitrophenol (Figure 1, right) is a persistent intermediate and precursor of several pharmaceutical drugs, pesticides, and dyes. The structure of both chemicals is similar to surfactants, therefore they can be considered as asymmetric polar compounds [9].

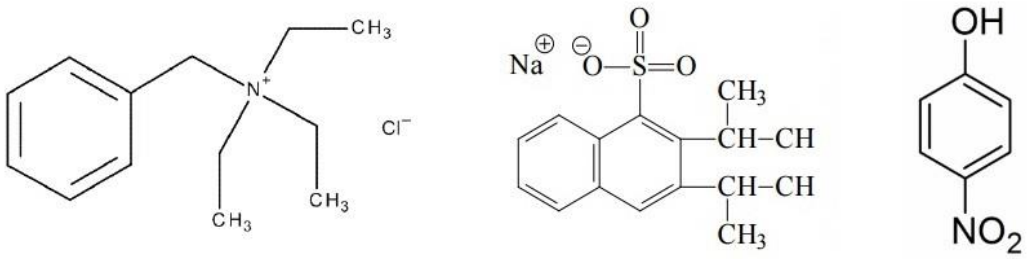

Figure 1. Chemical structures of TEBA (left), Supragil WP (middle) and 4-nitrophenol (right)

4-nitrophenol (pK_a = 7.15) can be present in non-ionic and anionic forms, depending on the pH of the supernatant. During the sorption process, 4-nitrophenol was present mainly in anionic form, but the measurement was carried out at the non-ionic form.

Experimental

Oil shale sample originated from Pula (Hungary), which was milled: ∅ < 0.8 mm.
Sodium alginate, agar, TEBA, Supragil WP, 4-nitrophenol and calcium chloride were purchased from Sigma-Aldrich Co., Naturtrade Hungary Kft., Merck KGaA., Rhodia Geronazzo Spa., Reanal Laborvegyszer Kft. and Lach-Ner, s.r.o., respectively. All chemicals were used without further purification.
UV-VIS measurements were performed on a Varian Cary 50 UV-VIS spectrophotometer, pH was determined with a Radelkis combination pH electrode.
The nonlinear least-square fitting procedure of the Origin scientific graphing and analysis software was utilized, using Levenberg-Marquardt algorithm.

Preparation of alginate beads

A solution of 2.5 % (w/v) concentration was prepared by dissolution of sodium alginate in deionized water. The obtained mixture was dropped into 0.2 mol/L $CaCl_2$ solution, and alginate beads were formed (∅: ~ 5 – 6 mm) instantly. After standing in the gelation media overnight, the beads were filtered out and washed with deionized water.

Preparation of oil shale–alginate beads

According to the above described procedure, sodium alginate mixture was prepared. This solution was mixed with the swollen oil shale, using 8 : 1 mass ratio of oil shale and sodium

alginate. This suspension was added dropwise into 0.2 mol/L $CaCl_2$ solution and oil shale composite beads were formed (∅: ~ 5 – 8 mm). The post-treatment is identical with that applied in the case of alginate beads.

Preparation of agar sorption layer
A solution of 0.66 % (w/v) concentration was prepared by dissolution of agar powder in boiling deionized water. Exact quantity of this mixture was poured into crystallizing dishes and cooled to room temperature.

Preparation of oil shale–agar sorption layer
According to the above described method, agar solution was prepared, and the semi-cooled solution mixed with swollen oil shale, using 30.3 : 1 mass ratio of oil shale and agar powder. This suspension was poured into crystallizing dishes and cooled to room temperature.

Sorption on oil shale powder
The sorption experiments were performed in 250 mL stoppered Erlenmeyer flasks. 5 g of oil shale powder was weighed into the flask and was left to swell in 5 mL water overnight at room temperature. Different concentrations of TEBA (from 2 to 20 mmol/L) or Supragil WP (from 50 μmol/L to 20 mmol/L) or 4-nitrophenol (from 50 μmol/L to 20 mmol/L) solutions were prepared with 0.01 mol/L $CaCl_2$ (pH= 7.4). 50-50 mL of these solutions were transferred to the swollen oil shale samples. The suspension was then shaken and left to stand for 24 hours for equilibration at room temperature. Then approximately 2 mL of the supernatant was transferred into an Eppendorf tube and was centrifuged at rpm = 15000 for 20 minutes for perfect separation of the supernatant and oil shale powder. After the centrifugation, the supernatant was measured by UV-VIS spectrophotometer and the concentration was determined.

Sorption on alginate and oil shale–alginate beads
The procedure to measure the sorption on alginate and oil shale composite was almost the same as in the case of the sorption on oil shale powder. In this case, instead of oil shale powder, the alginate beads or oil shale composite beads were weighed. The weighed oil shale–alginate composite beads contained 5 g of oil shale powder. The alginate content of the weighed oil shale composite beads was equal to the weighed alginate beads at these sorption experiments.

Sorption on agar and oil shale–agar sorption layer
The method to measure the sorption on agar and oil shale–agar layer was very similar to the above mentioned procedures. The exact quantity of cooled oil shale–agar suspension in crystallizing dishes contained 5 g of oil shale powder. The agar content of the weighed oil shale–agar layers was equal to the weighed agar layers at these sorption experiments. The incubation time in this case was 48 hours.

Before the 4-nitrophenol concentration measurement, the supernatants were diluted with 0.1 M HCl in 1 : 1 ratio in every case, for the more precise concentration determination.
All samples were in triplicate. The UV-VIS absorbance of the blank sample (c_0 = 0 mol/L) was subtracted.

Results and discussion

The adsorption isotherms were analyzed in terms of Langmuir or Freundlich isotherm equation, which ever fits on the data better.

Langmuir isotherm: $q_e = Q \cdot \frac{K_L \cdot c_e}{1 + K_L \cdot c_e}$

Freundlich isotherm: $q_e = K_F \cdot c_e^n$

where q_e is the adsorption capacity at equilibrium, mol of solute adsorbed per gram of adsorbent (mol/g); c_e is the equilibrium solution concentration (mol/L); Q is the maximum amount of solute adsorbed for monolayer coverage of the surface (mol/g); K_L is the Langmuir constant (L/mol); K_F ($L^n/(mol^{(n-1)} \cdot g)$) and n are Freundlich constants.

The adsorbed amount of the solute was calculated according to the following equation:

$$q = \frac{V \cdot (c_0 - c)}{m}$$

where q is adsorption capacity at equilibrium (mol/g); V is the volume of the equilibrium solution (0.05 L); c_0 and c are the initial and the equilibrium concentrations of the solute (mol/L); m is the weighed amount of the dry adsorbent (g).

The adsorption isotherms of TEBA and Supragil WP can be seen in Figure 2. In the case of TEBA, the amount sorbed by oil shale calculated from the oil shale–agar layer (**light blue line**) is almost the same as by oil shale powder (**black line**), while the amount sorbed by oil shale calculated from oil shale–alginate beads (**blue line**) is slightly lower than by oil shale powder. The diffusion of cationic TEBA to the oil shale is hindered through the negatively charged alginate in the composite, while the diffusion of TEBA is not hindered through the relatively neutral agarose gel.

In the case of Supragil WP, the amount sorbed by oil shale calculated from the oil shale-agar layer (**light blue line**) is lower than by oil shale powder (**black line**). It can be explained by the apolar-apolar interaction between Supragil WP and agar, which hinders the solute to reach the oil shale in the composite. The amount sorbed by oil shale calculated from oil shale-alginate beads (**blue line**) is higher than by oil shale powder. It can be caused by the difference of liquid-solid ratio compared the powder to the composite. Thus, the repulsion between the anionic Supragil WP and the anionic surface-charged oil shale powder is more significant.

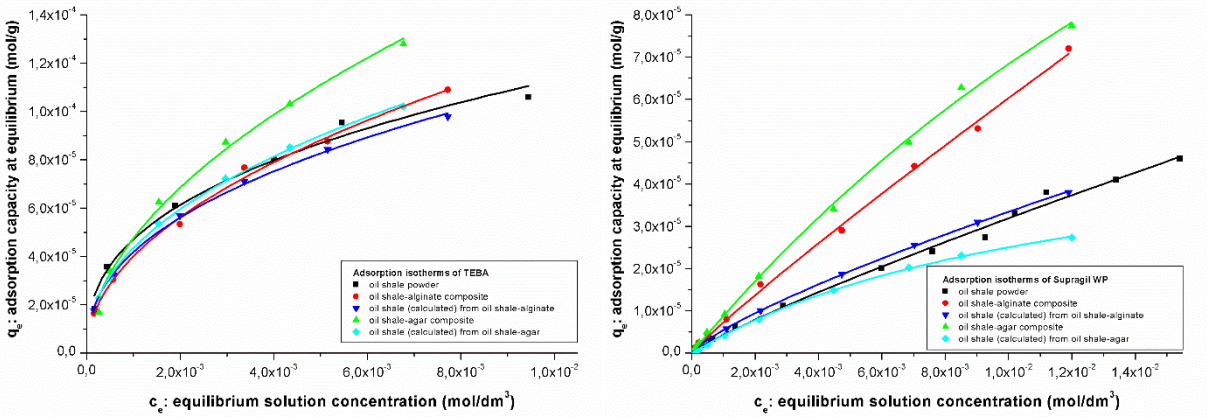

Figure 2. Adsorption isotherms of TEBA (left) and Supragil WP (right)

The tendency of adsorption isotherms of 4-nitrophenol is very similar to the adsorption isotherms of Supragil WP (Figure 3), although the sorbed amounts are higher in the case of 4-nitrophenol. During the sorption process, 4-nitrophenol was present not only in anionic form, but also in non-ionic (protonated) form. Thus, the electrostatic repulsion between the oil shale powder or the oil shale in the composite and 4-nitrophenol is less pronounced, which induces the higher 4-nitrophenol uptake of sorbents.

A comparison of the adsorption isotherms (Figure 3, right) demonstrates the sorption differences between the cationic TEBA, anionic Supragil WP, and, partly anionic 4-nitrophenol compounds. The sorption ability of TEBA is much higher than that of Supragil WP or 4-nitrophenol on the anionic surface-charged oil shale. The explanation is the electrostatic repulsion or attraction between the oil shale and the solute.

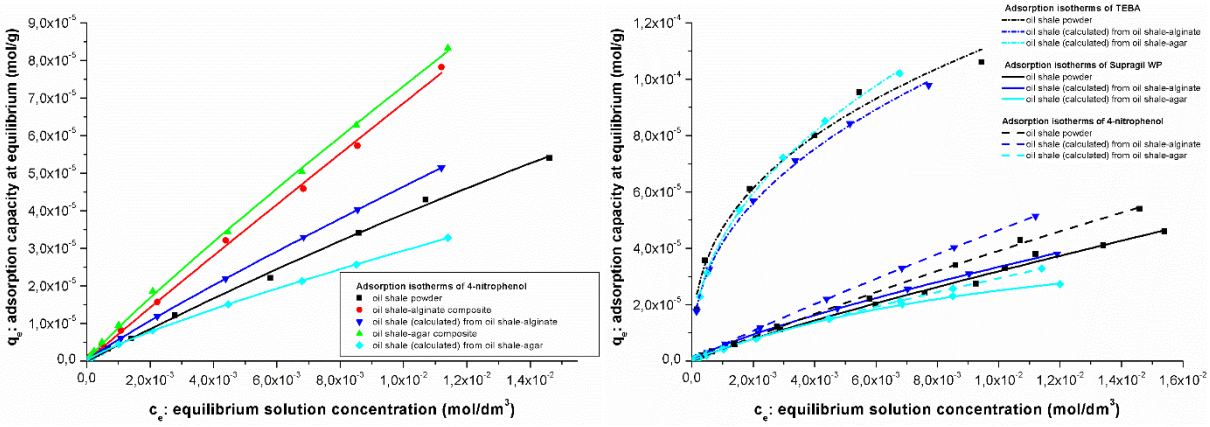

Figure 3. Adsorption isotherms of 4-nitrophenol (left) and comparison of adsorption isotherms of TEBA, Supragil WP and 4-nitrophenol (right)

Conclusion

In this present work, we tried to find some manageable forms of Hungarian oil shale, the sorption abilities of which are as good as or better than those of the oil shale powder. Alginate and agar are suitable forming agents to form a workable and efficient sorbent composite with oil shale for eliminating chemical pollutants. Identifying the physical and chemical properties of the actual contaminant to be eliminated from the environment, we can choose the best forming agent, which results in a more successful retention of pollutants.

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